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XRD Data Analysis Via Rietveld Refinement and Bandgap Studies of $PbTi_{0.95}Zr_{0.05}O_3$ Perovskite

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***Abstract*—Zr modified $PbTiO_3$, $Pb(Zr_xTi_{1-x})O_3$ (PZT) has been under extensive research during the last decades as it inherits considerable ferroelectric, piezoelectric and other electrical properties. In this piece of work, we report 5% Zr doped $PbTiO_3$ synthesized by solid state reaction route. The sample is nearly a single phased solid solution. The sample has been investigated for structural, optical bandgap and ac conductivity behaviour. The XRD data studies revealed tetragonal phase formation by the sample. The optical bandgap estimated from the Tauc's plot reveals a bandgap value of 3.1eV. Since the sample displays nearly the insulating bahaviour, its frequency dependent ac conductivity is relatively low**

***Keywords*—Lead Zirconium Titanate, Solid State Route, Crystal structure, Optical Bandgap, ac conductivity**

I. INTRODUCTION

$PbTi_{0.95}Zr_{0.05}O_3$ (PZT)is the most common ferroelectric (FE) material widely used in solid-state technology. It displays a strong piezoelectric property in polycrystalline form. The ferroelectric and properties along with better dielectric nature and wide band gap properties makes it favorable material to be used in transducers, ferroelectric FETs, sensors, actuators and non-volatile random-access memories [1-4]. Lead Titanate Zirconate ($PbZr_{1-x}Ti_xO_3$) solid solutions known as PZT crystallize to the various distorted perovskite structures. These materials have drawn considerable interest for material researchers due to its interesting ferroelectric, piezoelectric and other electrical properties. Such materials are often used in ultrasonic generators, hydrophones, electronic buzzers and ringers, pressure and stress sensors, etc. Since their discovery in the early 50's, $PbZr_{1-x}Ti_xO_3$, or PZT ceramics are recognized as excellent piezoelectric materials [5,6]. At room temperature, the solid solution between lead titanate, PbTiO $PbZr_{1-x}Ti_xO_3$ $PbZr_{1-x}Ti_xO_3$ (PT), and lead zirconate, PbZrO $PbZr_{1-x}Ti_xO_3$ (PZ), presents two ferroelectric phases, a tetragonal phase in the titanium rich side of the pseudobinary system, and a rhombohedral one in the zirconium rich side. This transition is usually classified as morphotropic because it corresponds to a structural change with the variation in composition [7,8]. In the thin films, PZT finds use in microelectro-mechanical-systems (MEMS), e.g., allows for the low voltage actuation as advantageous for gyroscopes, ultrasonic transducers or RF switches [9-11].

It is well known fact that all the physical and chemical properties of the sample depends on particle size, morphology, crystal structure and the processing conditions. Therefore, method of preparation is expected to influence the properties of the sample. Scientists have developed various synthesis techniques which include solid state route, sol-gel method, RF sputtering, Pulsed laser deposition and various others. Among these methods, solid state route ensures better sample formation, with higher possibility of the single phase-ness. It however requires high temperature treatment which may induce structural inhomogeneities [11-14].

In this project, we synthesized $PbTi_{0.95}Zr_{0.05}O_3$material by solid state route. The synthesized sample is characterized for structural, optical and conductivities properties. XRD technique was exploited for structural determination, DRS UV-Vis spectroscopy was employed for optical bandgap determination, and for conductivity studies, dielectric measurement was carried.

II. PREPARATIONS AND CHARACERIZATIONS

Synthesis

To synthesize $PbTi_{0.95}Zr_{0.05}O_3$material by solid state route, the precursors were PbO, TiO_2 and ZrO_2. All these oxide materials were used without pre-heating. The stoichiometric ratios calculated using on the molecular formula and weighed by a sensitive digital balance. The materials were mixed in the fixed ratio and were mechanically mixed using agate mortar and pestle for about 5h. The fine powder so obtained was calcined for 5h at 1000 ^oC. The same process was repeated once more. This is why the employed method is known as double calcination process. Duering grinding, acetone was used for proper dispersion of the precursors. The final powder was transformed into the pellets of the diameter of 10mm with 1mm thickness. The pellet was sintered at 1200 ^oC for 6h. The compact pellets so obtained was polished by silver oxide paste to form electrodes. This is done to carry out the dielectric measurements. Some powder form of the sample is retained for X-ray diffraction and optical bandgap measurements.

Characterizations

The sample was examined for structural studies using the most reliable X-ray diffraction technique in the angular range of $20^o \leq 2\theta \leq 80^o$. The XRD data was recorded by using a PROTO AXRD Benchtop Diffractometer with Cu-$K\alpha_1$ radiation (λ = 1.5406Å). The sample was subjected to optical bandgap studies using UV-Vis Diffuse Reflectance Spectroscopy (DRS). To

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analyze the dielectric properties, Keysight Technologies' Model E4980A Precision LCR meter was used. Here in this study, the dielectric data was converted by specific formula in to the ac conductivity of the sample. It is worth to mention here that all the characterizations were carries out at room temperature.

III. RESULTS AND DISCUSSIONS

XRD Data Analysis

For $PbTi_{0.95}Zr_{0.05}O_3$known as Zr doped Lead titanate**,** we investigated the crystal structure and parameters related to crystal structure using X-Ray diffraction (XRD) characterization. The study of the XRD patterns witness the acquisition of tetragonal structure with space group P4mm [15,16]. The structure and other related parameters were determined using Rietveld refinement employing FullProf software. The Rietveld refined XRD data of the as prepared sample is displayed as Figure1. Some diffraction peaks skip the Refinement as witnessed from Figure1. These peaks are the impurity peaks which may are attributed to the un-reacted $PbTiO_3$ phase.

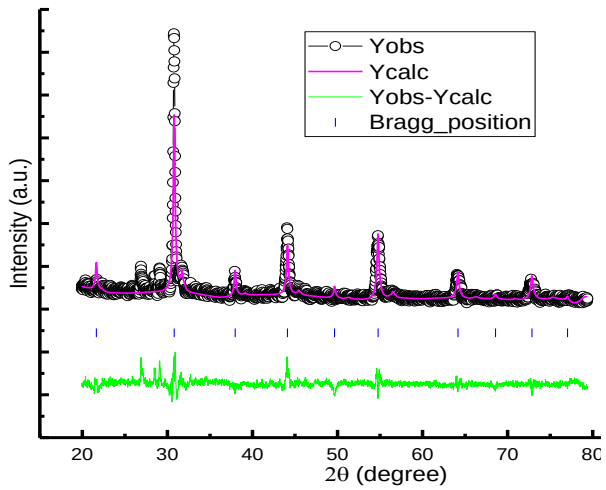

Fig. 1. Rietveld Refinement of X-ray data of $PbTi_{0.95}Zr_{0.05}O_3$ Perovskite.

Table 1: Structural parameters obtained from XRD via Rietveld refinement

S. No.	Parameters	values
1	Space group	P4mm
2	Crystal structure	Tetragonal
3	Lattice parameters	$a = b = 3.9980$ and $c = 4.10228$ (Å)
4	$\alpha = \beta = \gamma$	90°
5	Volume (Å^3)	69.04
6	Density(g/cm^3)	11.34
7	GoF	2.89
8	χ^2	2.77

The absence of background noise revealed the complete phase formation, whereas, high peak intensity with sharpness witness crystallinity and narrow FWHM of these reflections is evident of higher average crystallite size. The average particle size of the material was calculated via Debye Scherrer's equation and average size of particle was calculated to be 86 nm. Further, all the parameters related to the crystal structure and phase formation are documented in Table 1.

Optical Bandgap Studies

Room temperature Diffuse Reflectance UV-Vis spectroscopy (DRS) was exploited to throw light on the bandgap property of $PbTi_{0.95}Zr_{0.05}O_3$ material. The recorded DRS spectra has been converted into Kubelka–Munk functionand was plotted as $[F(R)*hv]^2$ (n= 2 for the direct band gap transition) against E(eV)and the plots are displayed as in Figure 2, commonly known as Tauc's plot. From this plot, band gap can be determined by extrapolating the linear portion of curve. The extrapolated line makes an intercept on energy axis and the magnitude of intercept is actually the band gap value. The energy band gap for the prepared sample was estimated to be 3.1eV. The bandgap value is literally lower than parent $PbTiO_3$ attributed to merging of an impurity band into the conduction band occurs which in turn shrinks the width of optical band gap. Further, it helps electrons to easy transfer from VB to CB. Besides this the interaction among the electrons and impurities would be the reason for reduction in width of electronic band gap [12-17].

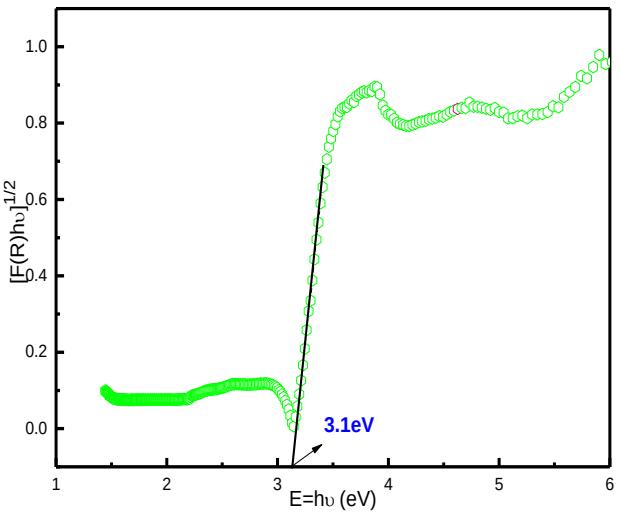

Fig. 2. Tauc's plot for Optical band gap estimation of $PbTi_{0.95}Zr_{0.05}O_3$.

Ac Conductiity Studies

The Figure 3 shows the behavior of ac conductivity against logarithm of frequency at room temperature. It has been illustrated that ac conductivity is nearly independent in the lower frequency sites and referred to as dc conductivity whereas ac conductivity starts to increase with frequency at region of higher frequencies. A possible explanation for this behavior is that, at the beginning, when doping is applied to the material, charge carriers barely move and are confined in the material. As the frequency increases, after a certain value the charge carriers start penetrating the barriers and de-trapped with that the conductivity increases. Increase in the field speed

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up the movement of electrons, resulting in a rapid increase in conductivity. Thereafter any increase leads to the enhanced values of the ac conductivity by the sample [16-19].

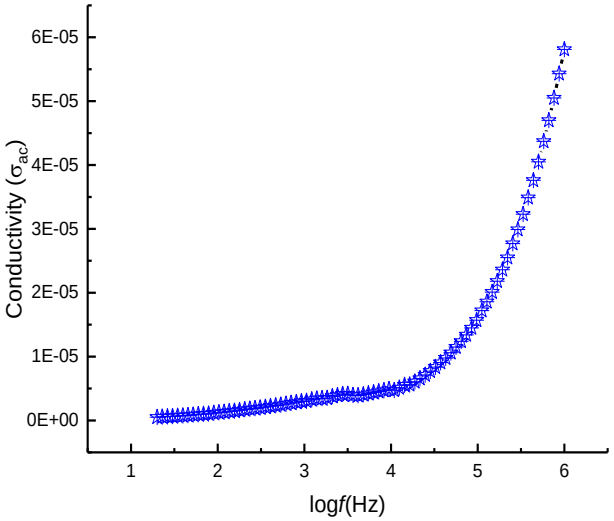

Fig. 3. *ac* conductivity as a response to the applied frequency of $PbTi_{0.95}Zr_{0.05}O_3$ Perovskite.

IV. CONCLUSION

The polycrystalline sample of $PbTi_{0.95}Zr_{0.05}O_3$ material was synthesized successfully by solid state reaction route**.** The tetragonal phase was witnessed from Rietveld refinement of XRD data of PZT. The particle size calculated using Scherer's formula was found to be 86nm. The traces of $PbTiO_3$ phase were witnesses which remains unfitted in the XRD diffractogram. The narrow FWHM and intensity of the reflections are witnessing the low particle size and the crystallinity of the sample. The optical bandgap from the Tauc's plot was estimated to be 3.1eV which can be tailored to fit for opto-electronic devices particularly in high-temperature and power switching applications. The conductivity is considerably low thereby witness the insulating nature of the sample.

Futue Implications

As $PbTi_{0.95}Zr_{0.05}O_3$ materials are better dielectric, piezoelectric, ferroelectric and exhibit wide band gap materials, it has potential applications in advanced technology. A pure crystal of PZT can be tailored from bandgap point of view to make it a strong candidate for RF signal processing, high-temperature and power switching applications and other optoelectronic device applications

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